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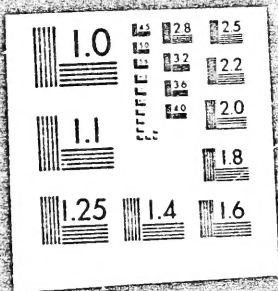
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METAL HYDRIDES FOR ENERGY STORAGE APPLICATIONS

S. C. Garg, et al

Civil Engineering Laboratory (Navy)
Port Hueneme, California

June 1975

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Technical Note N-1393

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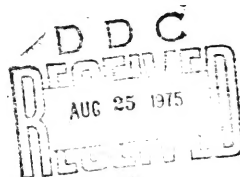S. C. Garg and A. W. McClaine

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TN-1393	2. GOVT ACCESSION NO. DN848127	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) METAL HYDRIDES FOR ENERGY STORAGE APPLICATIONS		5. TYPE OF REPORT & PERIOD COVERED Not final; 1 Jul 1973 – 30 Jun 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S. C. Garg A. W. McClaine		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Civil Engineering Laboratory Naval Construction Battalion Center Port Hueneme, CA 93043		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61152N; ZR000-01; ZR-022-06; Z-R000-01-139
11. CONTROLLING OFFICE NAME AND ADDRESS Director of Navy Laboratories Washington, DC 20376		12. REPORT DATE June 1975
		13. NUMBER OF PAGES 60
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

thermal insulation; heat transfer; heat sinks; energy storage systems; closed ecological systems

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A survey was made of metal hydrides for energy storage in the form of hydrogen, heat, and a combination of both. Five intermetallic compounds were found to be promising energy storage vehicles. They were: $MgNi$, $FeTi$, $LaNi_5$, $La_{0.3}Ni_5$, and Mischmetal Ni_5. The most important property common to all these hydrides is their ability to store large quantities of hydrogen per cubic foot of the hydride: between 5 and 7 pounds per cubic foot, compared to a liquid hydrogen density of about 4.4 pounds per cubic foot. Each of these compounds

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was found to be able to store hydrogen under different experimental conditions, and each has its unique properties and handling characteristics.

The survey was followed by a consideration of areas of possible useful applications. Several areas where metal hydrides can be of use are discussed in detail, including energy storage at remote bases and combat zones, underwater fuel storage, fuel and heat storage in closed system operations, and their use in heat pumps and automotive applications. Because of the ability of metal hydrides to supply hydrogen and absorb exhaust heat at the same time, and to deliver this absorbed heat during recharging where it can be used, they are useful in achieving better utilization of available energy.

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METAL HYDRIDES FOR ENERGY STORAGE APPLICATIONS,
by S. C. Garg and A. W. McClaine

TN-1393   56 p. illus   June 1975   Unclassified

1. Thermal insulation   2. Heat transfer   3. Heat sinks   I. Z-R000-01-139

A survey was made of metal hydrides for energy storage in the form of hydrogen, heat, and a combination of both. Five intermetallic compounds were found to be promising energy storage vehicles. They were $MgNi$, $FeTi$, $LaNi_5$, $La_{0.7}Ce_{0.3}Ni_5$, and Mischmetal Ni_5. The most important property common to all these hydrides is their ability to store large quantities of hydrogen per cubic foot of the hydride: between 5 and 7 pounds per cubic foot compared to a liquid hydrogen density of about 4.4 pounds per cubic foot. Each of these compounds was found to be able to store hydrogen under different experimental conditions, and each has its unique properties and handling characteristics. The survey was followed by a consideration of areas of possible useful applications. Several areas where metal hydrides can be of use are discussed in detail, including energy storage at remote bases and combat zones, underwater fuel storage, fuel and heat storage in closed system operations, and their use in heat pumps and automotive applications. Because of the ability of metal hydrides to supply hydrogen and absorb exhaust heat at the same time, and to deliver this absorbed heat during recharging where it can be used, they are useful in achieving better utilization of available energy.

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INTRODUCTION

In considering alternate fuels for future Navy use, hydrogen stands out as a fuel with great potential in terms of usefulness, availability, and product emissions. Hydrogen can be used in both internal and external combustion engines; it can be burned for heating purposes; and it can be used in fuel cells. It is a component of water which is available everywhere. Finally, the products of combustion with air are water and some oxides of nitrogen (oxides of nitrogen are products whenever combustion is sustained with air at high temperatures).

One of the greatest problems with hydrogen is its low energy density. As a gas at atmospheric pressure, hydrogen has an energy density of 29% of that of natural gas. As a liquid stored at cryogenic temperatures, hydrogen has an energy density of 28% of that of gasoline. These low energy densities present inconveniences when mobility of the fuel is a concern.

In recent years much work has been done on the chemical storage of hydrogen in metal hydrides. Energy densities of up to 40% of that of gasoline appear possible. Energy densities at least as high as that of liquid hydrogen have been demonstrated and without the problems that accompany liquid hydrogen.

The purpose of this study was to determine what metal hydrides are available, and how applicable they might be to Navy needs. A survey and compilation of the metal hydrides was carried out, and then a short look was taken into various uses of this type of storage.

COMPARISON OF ALTERNATE FUELS AND HYDROGEN STORAGE METHODS

In the classification of chemical energy storage many possible fuels reveal themselves. These possibilities take the form of synthetic fuels and include methane, methanol, ethanol, ammonia, synthetic gasoline, hydrazine, and hydrogen. Table 1, taken from Reference 1 compares several of these fuels.

Two of these chemical alternatives--hydrazine and ammonia--must be used with great care because of the great danger if they are released in the air. These fuels have extremely low maximum allowable concentrations of 1 ppm for hydrazine and 100 ppm for ammonia in air [2]. In addition, hydrazine is very dangerous to handle, except when diluted with water in which case it makes an excellent fuel for fuel cells but not for combustion processes [1].

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Table 1. Comparison of Storage Properties of Various Fuels[a]

Fuel Grade	SI (Metric) Units						Conventional Units					
	Density	Energy Density		Amount Equivalent to 20 Gallon Gas			Density	Energy Density		Amount Equivalent to 20 Gallon Gas		
	(kg/cu m)	(J/kg × 10³)	(J/cu m × 10⁵)	Liters	kg (fuel)	kg (tank/fuel)	lb/cu ft (60 F)	Btu/lb	Btu/cu ft	gal	lb (fuel)	lbm (tank/fuel)
Typical gasoline	702	44,380	311,700	75.7	53.1	63	43.8	19,050	835,700	20.0	117	150
Methane gas (CH₄, 1.38 × 10⁷ N/sq m)	114	50,000	56,850	415	47.2	500	7.09	21,500	152,400	110	104	1,100
Liquid propane (LPG, 6.89 × 10⁵ N/sq m)	510	44,400	236,000	100	51.1	85	31.8	19,900	632,800	26.4	112	180
Methanol (anhyd CH₃OH)	797	20,100	160,200	147	117	141	49.7	8,640	429,400	38.9	258	310
Ethanol (anhyd C₂H₅OH)	795	26,860	213,700	110	88.0	107		11,550	572,900	29.2	194	235
Liquid hydrogen (at NBP)	71	120,900	85,900	275	19.5	136	4.43	51,980	230,300	72.6	43.0	300
Hydrogen gas (1.38 × 10⁷ N/sq m)	1.07	120,900	12,920	1,820	19.5	2,090	0.667	51,980	34,650	482	43.0	4,600
Metal hydride (Mg₂NiH₄)	1,760	10,100	179,000	132	233	284	110	4,350	479,900	34.8	513	629
Liquid ammonia (at MBP)	771	18,600	143,500	164	127	152	48.1	8,000	384,800	43.3	279	335

[a] From Reference 1, "What are the possibilities for synthetic fuels," Automotive Engineering, which is based on talks presented at the "Energy and the Automobile" session held at the National Automobile Engineering Meeting, May, Detroit. Reprinted with permission: "Copyright Society of Automotive Engineers, Inc., 1973, all rights reserved."

The other fuels can be synthesized in various ways, at various costs. Synthetic gasoline appears to require the most steps and provides no benefits in terms of reduced air pollution over the present oil derivative. Methane, methanol, and ethanol are all presently being studied and have been shown to be cleaner burning than gasoline [3, 4, 1]. Methane can be compressed or liquified and as such is subject to all the problems inherent with pressurized gas or cryogenic liquids. In terms of energy densities methanol and ethanol will take up 2.2 and 1.7 times more weight and 1.9 and 1.5 times more volume than gasoline. This appears to be their only major problem though, and several recent articles indicate that prices will shortly be competitive with gasoline [3, 4].

The last major contender as a synthetic fuel is hydrogen. Hydrogen is a major constituent in many of the other fuels and in most cases must be supplied during their synthesis processes. Hydrogen is more of a universal fuel than the others. It can be burned efficiently and with very low emissions in either internal or external combustion engines. It can be used for cooking and heating; and since the exhaust products are water and air and would not need to be vented, one should expect a heating efficiency of 100%. Finally, it is an excellent fuel for fuel cells. In short, hydrogen is the superior fuel. It can be prepared in numerous ways, including electrolysis [5], steam reformation, and chemical cracking [6]. Its only major problem is its storage.

Four methods presently exist for storing hydrogen:

1. It can be stored as gas in huge containers at ambient temperatures and low pressures.

2. It can be stored as gas compressed to very high pressures of the order of 2,000 to 7,500 psia (135 to 510 atmospheres).

3. It can be liquified to reduce further the storage volume.

4. It can be stored chemically bonded in metallic and intermetallic hydrides.

The first case would serve well where space is unimportant. In situations where mobility is important, or where space is limited the volume would have to be smaller. The pressurized hydrogen storage does not present a significant improvement over the first storage method because of the excessive weight of pressure vessels required for storage, and the amount of energy needed to compress the hydrogen. Liquifying hydrogen is a good method in terms of weight and volume, but it requires a large expenditure of energy to first liquify it and then, when needed, to gasify it (an amount of energy equivalent to about one-third of the energy stored in the hydrogen). Further disadvantages are the large amount of equipment needed to transport and transfer the cryogenic hydrogen and the short period that liquid hydrogen can be stored before it vaporizes in its container and must be vented.

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The final method, the storage of hydrogen in chemical bonds in metallic and intermetallic hydrides, shows great promise for avoiding the problems of the other three methods. The Billings Energy Research Corporation in Provo, Utah [7, 8] has recently demonstrated an experimental iron-titanium hydride storage unit. This unit absorbs hydrogen at pressures of 150 to 1,030 psia (10 to 70 atmospheres) and at temperatures of 100°F to 150°F. During the absorption of the hydrogen, heat is given off.[a] Then, as hydrogen is burned in an automobile engine, for instance,[a] the exhaust heat from the combustion is used to release the hydrogen from its hydride bonds. Iron-titanium hydride is now a proven energy storage material.

Figures 1a, 1b, and 1c compare pressurized, liquified, and metal-hydride hydrogen storage systems in terms of extimated cost, weight, and volume, respectively. Where volume is a consideration the metal hydrides are definitly applicable systems. Where weight is the prominent consideration liquid hydrogen appears to be the best choice. Where cost is the major factor it is uncertain which system would be best.

One further advantage of metal hydrides is that the energy used to dissociate the hydrogen from the hydride is not lost but can be utilized during the recharge period to heat buildings or water or to provide the heat needed for an absorption cooling system. Thus, more of the energy stored in the hydrogen can be used with a hydride system than would be used if the hydrogen were merely burned and the products exhausted. Less energy is used to compress the hydrogen in the hydride system than in the high pressure systems because the pressures are lower. Finally, the hydrides can store hydrogen indefinitely as long as they are isolated from deactivating substances. This is much superior to the liquified hydrogen schemes which can only claim to store hydrogen for a few days [7].

In short, metal hydrides appear to be useful energy storage vehicles in certain situations. Requirements such as utility life, shelf life, maintenance and cost effectiveness must be considered for each application. Once these requirements are known, the proper fuel and storage vehicle can be chosen. The following sections of this report attempt to present a general overview of the hydrides available and how they meet the requirement categories mentioned above.

CLASSIFICATION OF HYDRIDES

A short summary of the classification of metal hydrides, is included here only for completeness. More detailed descriptions are given in several publications, including References 9 and 10. Generally, hydrides are classified by the nature of the hydrogen bond into three principal categories:

- covalent or volatile
- saline or ionic
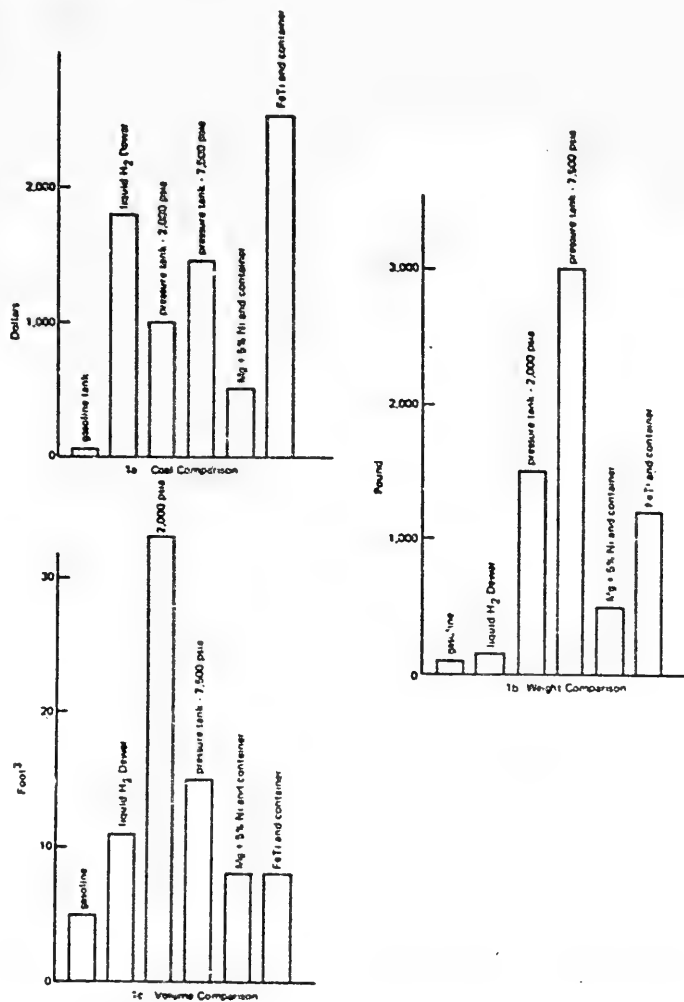- metallic.

[a] As in the Billings demonstration.

4

Figure 1. Comparison of cost, weight, and volume of hydrogen containers holding 21 pounds of hydrogen.

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Covalent or Volatile Hydrides

In covalent hydrides, the bond between hydrogen and the element is a nonpolar electron-sharing type where valence electrons are shared on a fairly equal basis between the elements held by the bond. Large differences in electric charges do not exist. In general, molecules of covalent hydrides are not strongly attracted to each other, and this absence of strong intermolecular forces results in the high degree of volatility and low melting point of the covalent hydrides. These hydrides are generally thermally unstable, such instability increasing with increasing atomic weight of the parent element. For the most part, these hydrides are extremely toxic and burn readily in the air or oxygen with liberation of considerable quantities of heat. Some of the elements which form covalent hydrides are: boron, aluminum, gallium, indium, thallium, silicon, and germanium.

Saline Hydrides

Saline hydrides are formed by the reaction of the strongly electropositive alkali metals and the alkaline-earth metals with hydrogen, which becomes strongly electronegative. The bonds of the saline hydrides result from the strong electrostatic forces existing between the dissimilar electric charges of the two ions. Therefore, saline hydrides are highly polar. These saltlike hydrides are crystalline, exhibit high heats of formation, and high melting points. The saline hydrides are more dense than the parent elements because of strong attraction between the metal and the hydride ions and, for the alkali metal hydride, because of the more efficient packing of atoms. With the exception of magnesium and beryllium, all alkali and alkaline-earth metals form saline hydrides. These two exceptions are frequently classified as covalent hydrides because some of their characteristics resemble covalent hydrides. Saline hydrides decompose when heated to moderately high temperature, giving off hydrogen. The saline hydrides are considered important reducing agents, and they are useful in the descaling of metals. They react with water and liberate hydrogen very readily. However, because the dissociation pressure of saline hydrides at temperatures to over $800^{\circ}F$ is less than atmospheric, they are not useful for the hydrogen storage applications under consideration.

Metal Hydrides

Metal hydrides are formed by the transition metals. They generally exhibit metallic properties: high thermal conductivity, high electrical resistivity, hardness, luster, etc. Unlike metals, however, they are quite brittle.

Metallic hydrides are generally formed by the absorption of hydrogen by the metal, resulting in compound formation. Compound formation is evidenced by invariant equilibrium pressures at constant temperature as hydrogen content changes over a certain range of compositions.

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The nature of the chemical bonding in the metallic hydride is still not well understood. There are three different models to explain the bonding of the hydrogen in these hydrides. However, none of the three models is completely satisfactory. The first model assumes that the hydride is an alloy of hydrogen and the metal, where it exists essentially as a proton in the hydride lattice. The second model is based on a predominantly covalent bond between the metal and hydrogen. The third model is essentially the converse of the first; the hydrogen exists as anions formed by removal of electrons from the metal to give a partially ionic bond.

Hydrogen dissolves in, or forms a compound with, metals either exothermally or endothermally. Those which react exothermally form a hydride phase by direct combination of metal and hydrogen. This class includes (1) the alkali and the alkaline-earth metals, which were not considered to be suitable for hydrogen storage applications under consideration because the hydrogen pressure at temperatures to $800^{\circ}F$ is below atmospheric; (2) the titanium and vanadium subgroup metals; (3) the rare earth (including scandium and yttrium); and (4) the actinide series metals and palladium. Most other metals (e.g., Fe, Co, Ni, Cu, Ag, and Pt) dissolve hydrogen endothermically. At low concentrations, the solubility of hydrogen in all metals so far studied is proportional to the square root of the hydrogen pressure. In exothermic absorbers at low temperatures and high pressures, the amount of hydrogen dissolved approaches compositions corresponding to stoichiometric hydride compounds. The crystal lattice of the endothermic absorbers is seemingly unaffected by the solution of hydrogen, whereas a change in lattice is common for the exothermic absorbers.

Recently, intermetallic compounds have been discovered which readily absorb and release large quantities of hydrogen per cubic foot of the compound. In the following survey, hydrides of the pure metals are first reviewed, followed by the hydrides of intermetallic compounds.

LITERATURE SURVEY

General

A search of available documents and summaries of programs underway at the present time under federal government sponsorship was carried out through the data bank search services of the Defense Documentation Center (DDC) and the National Technical Information Service (NTIS). Additional information was obtained during personal visits to the Brookhaven National Laboratory [11], and the Denver Research Institute [12]. These searches supplemented the more traditional literature search methods of reviewing technical publications and journals.

One of the reports obtained through NTIS turned out to be a bibliography of 358 publications on metal hydrides [13]. Based upon the titles, 108 of these references were considered to be of possible value

in the search for metal hydrides for hydrogen storage. A review of abstracts of these 108 reports, published in Chemical Abstracts and Nuclear Science Abstracts, was considered adequate as a first step in screening out those not pertinent to the application under consideration. For this reason, listing of all these references in this report was considered unnecessary.

This screening procedure showed that a majority of these publications dealt with hydrides useful in nuclear reactor applications as shields, controls, moderators, and reflectors. Some of the properties of metal hydrides, such as their stability over wide ranges of temperature and pressure, that makes them useful in nuclear reactor applications, also prevent their usefulness in hydrogen storage applications. These aspects of metal hydrides are dealt with more fully later.

Most of the documents and reports selected from the DDC Data Bank dealt with the application of hydrides in propellants and are not applicable to this report.

General information on metal hydrides given in this report for completeness was obtained from several sources [9, 10, 14]. A summary of metal hydrides which cannot be used for hydrogen storage applications and a discussion of the properties which prevent their usefulness are also included in this survey to indicate the limited number of hydrides which can be used for hydrogen storage.

Desirable Properties of Metals for Hydrogen Storage Applications

To determine which metals can be considered for hydrogen storage it is first necessary to outline the required properties of metals and their hydrides. These can be established fairly easily by considering a typical application: hydrogen generated by the electrolysis of water, using electrical energy either generated by nuclear reactors during off-peak hours [5, 15, 16] or generated by conversion devices powered by solar or wind energy or by the energy of ocean-currents [17, 18]. The hydrogen thus generated is to be stored for use sometime in the future and/or at locations or in equipment away from the source. If the hydrogen is to be used to generate electricity in central power-generating plants or in plants located at or near the consumer's location, the hydrogen can be transported either as a gas, using conventional pipelines, or as a liquid, using specially designed pipelines for cryogenic liquids, and then stored in appropriate storage tanks.

However, if the hydrogen is to be used in transportation applications (e.g., land moving vehicles or in applications requiring portability and relatively long storage times) neither of the above two transportation and storage methods is completely satisfactory. A list of desirable properties of metal-hydrogen systems is summarized below.

1. Most of the hydrogen present in the metal hydride should be recoverable when the pressure is reduced to atmospheric. The temperature required to liberate most of all the hydrogen present in the hydride should be at or above ambient but well below the exhaust temperature of the hydrogen combustion device used in the application.

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2. The hydride should have good kinetics of operation. It should be able to absorb and desorb hydrogen at a rate consistent with its use.

3. The metal should be able to store hydrogen for long periods at ambient temperatures that may range between $-20^{\circ}F$ and $+120^{\circ}F$.

4. The density of hydrogen in th. metal-hydrogen system should be quite high to keep the weight and volume of the storage tank down to a practical level.

5. The hydrogen storage system should be capable of thousands of cycles of absorption and desorption of hydrogen.

6. The operating temperatures and pressures during the absorption and desorption cycles should be well within the capabilities of today's most abundant storage container materials.

7. The hydrogen absorption process should be exothermic. The heat of dissociation should be low so that the heat exchanger is of a manageable size. The temperature of dissociation should be below the waste heat generated during the combustion of hydrogen in the energy conversion device so that the latter can provide the necessary thermal energy for the heat of dissociation.

8. The metal and its hydride should be nontoxic and should resist spontaneous combustion when brought in contact with air or oxygen.

9. The metal should be inexpensive to produce and widely available in large quantities.

10. The overall environmental effect of using a metal hydride to store hydrogen should be neutral or positive compared to the environmental effects of using other fuels. The effects of mining and processing the metal hydride and manufacturing the container must not outweigh the neutral effect of using hydrogen as a fuel.

All the above properties of a suitable metal-hydrogen system are fairly obvious with the possible exception of number 7. Metals which react with hydrogen endothermally are not suitable for hydrogen storage applications because heating the metal is necessary for the absorption of hydrogen, which is subsequently released upon cooling. In such systems, the solubility of hydrogen in the metal increases with increasing temperature. Therefore, only those metal-hydrogen systems which absorb hydrogen exothermally may be useful for hydrogen storage applications. Furthermore, unless the metal-hydrogen system is to be considered only for a limited number of specialized applications, it will be necessary that the metal-hydride system be relatively inexpensive and available in large quantities without causing unacceptable strains in the nation's economy and its resources.

The above listed properties should be considered for any situation. However, the specific application may require that some properties be given more emphasis than others. For instance, a remote base which is

using the metal hydride to store energy derived from wind, sun, and sea might stress items 1, 2, and 3 so as not to waste any hard-won energy. A combat-zone application might stress item 4 because of the need for mobility and invisibility. In the writing of this report certain hydrides were screened because they were either too stable, they were overly dangerous, or their operating temperatures and pressures were much greater than other available hydrides. The metallic hydrides considered are listed in the text. Intermetallic hydrides that were considered are listed in Table 2.

Properties of Hydrides

Important properties of each metal-hydrogen system may now be examined to see if they fulfill the above requirements.

As indicated earlier, hydrides of interest for our purpose are exothermic; i.e., heat is evolved when hydrogen is absorbed. These hydrides are almost always reversible, and the hydrogen can be recovered by lowering the pressure below, or raising the temperature above, the pressure and temperature required for the absorption process.

The behavior of a metal-hydrogen system may be described using the pressure-temperature-composition characteristics. The characteristics of a typical (albeit slightly idealized) metal-hydrogen/metal-hydride system are shown in Figure 2. Starting at the lower left-hand corner with the pure metal, as hydrogen is taken up by the metal and the atomic ratio H/M increases, the equilibrium pressure increases steeply until point A is reached. Up to this point the solid consists of a solution of hydrogen in metal rather than a compound. As the concentration is further increased by supplying more hydrogen, a second phase appears, having the composition B; and the addition of further hydrogen does not cause a further increase in pressure until all the solid phase has attained this composition. Above this plateau region, further enrichment of the solid by hydrogen requires a steep increase in pressure. The curves labeled T_1, T_2, and T_3 in Figure 2 show the effect of temperature on the pressure-composition relationship.

At a given temperature, therefore, each hydride is in equilibrium with a definite pressure of hydrogen, (called its decomposition pressure) which also depends upon the quantity of hydrogen in the metal. In the two-phase region, between A and B, at a given temperature, the decomposition pressure is independent of hydrogen concentration in accordance with the phase rule. In the single-phase region, below point A and above point B, the decomposition pressure varies with both temperature and hydrogen concentration. These relationships hold irrespective of the nature of the solid present.

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Table 2. Intermetallic Hydrides Included in the Literature Survey

Hydride	Wt % H_2	Reference	Problems
Mg + 6% Ni	6.97	[32]	—
Mg + 9% Cu	6.62	[56]	—
FeTi	0.87-1.81	[57]	—
$LaNi_5$	1.54	[58]	—
$LaNi_4Cu$	1.14	[28]	—
$LaNi_{2.5}Cu_{2.5}$	0.68	[28]	—
$LaNi_2Cu_3$	0.45	[28]	—
$LaNiCu_4$	0.33	[28]	—
$LaMg_{8.5}$	5.3	[38]	pyrophoric
$LaFe_5$	0.62	[28]	too stable
$LaCu_5$	0.48	[28]	too stable
$La_{0.7}Ce_{0.3}Ni_5$	1.6	[58]	—
$PrCo_5$	0.76	[28]	—
$CeMg_{8.5}$	4.5	[28]	pyrophoric
Y_5Mg_{24}	4.8	[28]	pyrophoric
$CeFe_5$	0.69	[28]	too stable
$PrCu_5$	0.57	[28]	too stable
$Pr_{0.8}Ce_{0.3}Cu_5$	0.42	[28]	too stable
$NdCu_5$	0.66	[28]	too stable
$CeCo_5$	0.58	[59]	—
$SmCo_5$	0.67	[59]	—
$MmNi_5$[a]	1.5	[28]	—
ZrNi	1.0	[60]	—
TaV	0.35	[61]	—
NbV	1.11	[61]	—
Mg[b]	7.66	[26]	—
V[b]	1.94	[62]	—
Nb[b]	0.85	[62]	—
Pd[b]	0.57-0.66	[9]	—

[a] Mm is mischmetal.

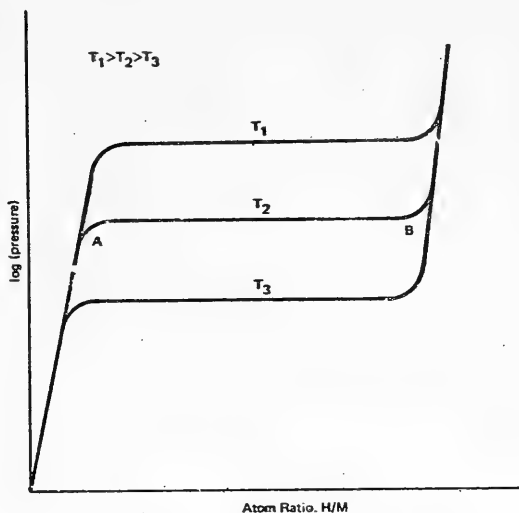[b] Metallic hydrides included for comparison.

Figure 2. Typical pressure-composition diagram for a ___al-hydrogen system.

Several factors determine the rates of hydrogen-metal reaction. First of all, the nature of the system itself is a strong determinant of the reaction rate. Certain alloys react almost as fast as the hydrogen can be supplied, whereas others react very slowly. Second, the cleanliness of the metal surface determines the rate of reaction. An oxide film, for example, will often slow down the reaction rate at first. Third, the smaller the particle size the faster will be the reaction rate. This is not too surprising since the larger the surface area of a given amount of solid, the higher should be the diffusion rate. Finally, the rate of reaction can be increased by the addition of a small amount of catalyst. This will be dealt with in more detail later.

Hydrides having high dissociation pressures are less stable than those with lower dissociation pressures. For most hydrides, the logarithm of the dissociation pressure decreases in a linear manner with the reciprocal temperature, viz,

$$\text{Log}_{10} p_H = -\frac{A}{T} + B$$

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Libowitz [19] plotted the logarithm of the dissociation pressure for a number of metal hydrides taken from a number of publications, including References 20 through 26 and found the above relationship to be accurate. Figures 3a, b, and c show several of these plots.

At temperatures below about 700°F, some hydrides exhibit hysteresis on their pressure-temperature-composition diagrams. For a given fixed temperature, the equilibrium pressure is higher during absorption than during desorption for the same composition. Typically, this behavior is illustrated in Figure 4. Several theories have been offered for hysteresis [19], but none of them have been satisfactory in explaining all the observed phenomenon.

In order to evolve hydrogen for use as a fuel, the pressure in the fuel supply line must be lowered below the dissociation pressure corresponding to the temperature of the stored hydride bed. The rate of hydrogen evolution is dependent upon the difference between the actual hydrogen pressure and the equilibrium dissociation pressure. The heat of dissociation must also be provided; and, depending upon the geometry of the heat transfer surface, the heat transfer rate can limit the rate of hydrogen evolution. The waste heat of the internal combustion engine provides an excellent source for the heat of dissociation, the exhaust temperature being anywhere between 600° and 1,400°F, depending upon the load and speed.

Hydrides of Pure Metals

The grouping of elements below is based upon their position in the periodic table. Because of the cost, availability, and safety considerations, radioactive elements will not be considered here for hydrogen storage for the applications under consideration.

Lithium, Sodium, Potassium, Rubidium, and Cesium. The alkali metals absorb hydrogen readily and violently. All elements in this group compress upon hydrogenation. The volumetric percentage compression ranges between 21.5% for lithium to 44.6% for cesium. These hydrides are very reactive, the reactivity depending upon the degree of solubility of the reaction products in the reaction medium. They are very reactive with water, which makes them difficult to handle. All alkali metal hydrides require temperatures above 800°F for hydrogen generation at atmospheric pressure [10, 20, 24]. Because of the high temperature requirements and high reactivity with water, the alkali metals are not suitable for hydrogen storage applications.

Beryllium, Magnesium, Calcium, Strontium, and Barium. Beryllium hydride cannot be obtained by direct synthesis from elements [9], and, therefore, it is not suitable for the application under consideration. The dissociation pressures of the hydrides of calcium [29], strontium [30], and barium [31] are well below atmospheric even when temperatures exceed 1,000°F. These metals, therefore, cannot be considered for hydrogen storage.
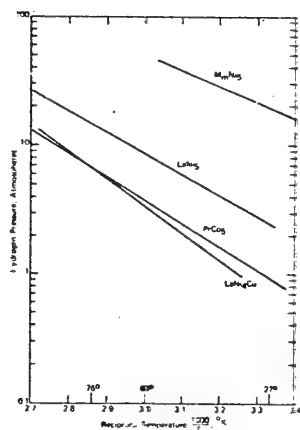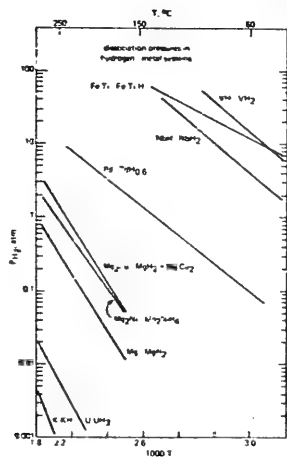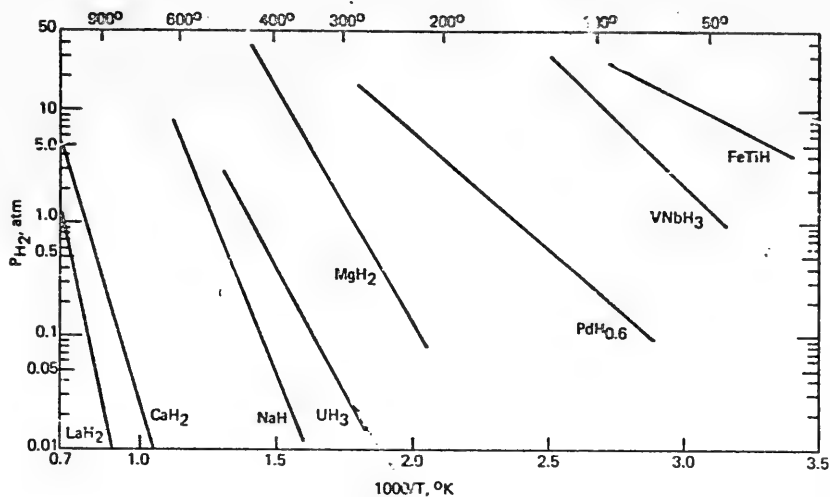
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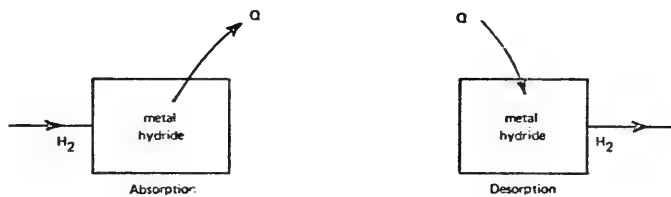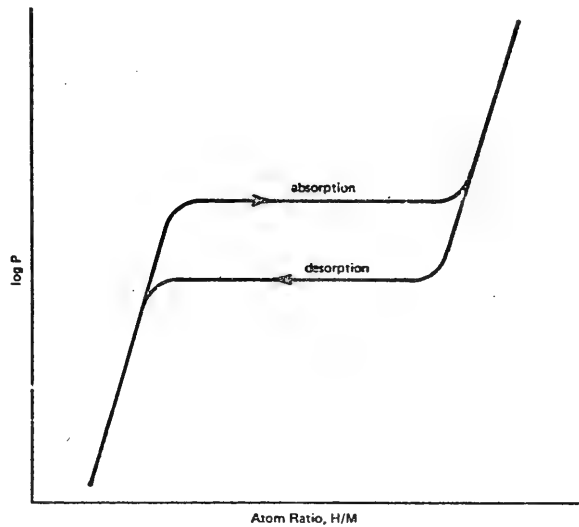Figure 3. Dissociation pressures of metal hydrides.

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Figure 4. Hysteresis in metal-hydrogen systems.

Magnesium on the other hand appears suitable for hydrogen storage. Its dissociation pressure at 547°F is 14.7 psia. To obtain high dissociation pressures, the temperature of the hydride will have to be raised. For instance, temperatures of 705°F and 800°F will provide dissociation pressures of 10 and 30 atmospheres, respectively [26]. The stoichiometric composition of the magnesium hydride that is formed corresponds to MgH_2, and almost all of the hydrogen is available as the pressure is reduced and the temperature of the hydride is increased.

Magnesium is inexpensive, about $1.00 per pound and widely available in nature. Magnesium hydride has a density of 1.42 gm/cc and contains 7.65% by weight of hydrogen, 93% of which is readily available. The volumetric density of hydrogen in the magnesium hydride, assuming 60% void fraction, is 485 cubic feet per cubic foot of the hydride. The heat of dissociation required to release hydrogen from magnesium hydride is about 25% of the heat of combustion of hydrogen [11], which is excellent in view of the fact that this is much less than the heat that will normally be wasted as exhaust in any combustion process involving hydrogen.

The density of hydrogen in magnesium hydride may be compared with the density of liquid hydrogen at boiling point. If 60% void fraction is assumed in the hydride, the density of recoverable hydrogen in it is about 2.71 pounds per cubic foot, which is approximately 61% of the density of liquid hydrogen of 4.42 pounds per cubic foot. In view of the fact that no cryogenic temperatures are involved and handling boil-offs is not required the density of hydrogen in magnesium hydride is excellent.

The major disadvantage in the use of magnesium for hydrogen storage appears to be in its very slow reaction with hydrogen. This problem has been overcome by J. J. Reilly and R. H. Wiswall, Jr. [32], by the use of nickel as a catalyst. Since the addition of nickel to magnesium makes it an intermetallic compound, it will be discussed in detail in the Hydrides of Intermetallic Compounds section of the report.

Scandium, Yttrium, and the Rare Earth Elements. Scandium hydrogen and yttrium-hydrogen systems are unsuitable for hydrogen storage. The scandium-hydrogen system has been studied in detail by Beck [33] and Lieberman and Wahlbeck [34] and was found to be very stable, with dissociation pressure below the atmospheric pressure even when the temperature was raised to over 1,800°F. Similarly, the dissociation pressure for the yttrium-hydrogen system has also been found to be below atmospheric [25, 35] at temperatures to 1,800°F.

Studies of the rare-earth/hydrogen systems have been carried on more or less continuously since the beginning of this century. However, since the rare earths are somewhat difficult to separate from one another, much of the work was done on mixtures of rare-earth metals. These mixtures have been described as lanthanum ''mischmetal,'' cerium mischmetal, etc., depending on the particular rare-earth metal that predominates the composition.

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Because of their similarity, the rare-earth metals would be expected to have similar hydriding characteristics. With the exception of europium and ytterbium, all the rare-earth metals form dihydrides that readily absorb additional hydrogen to form trihydrides. Ytterbium forms trihydride with difficulty under high pressures whereas europium does not form a trihydride at all [36].

Based upon the available experimental data in References 29 and 37 through 43, however, the rare-earth hydrides are not suitable for hydrogen storage applications because, to extract hydrogen out of their hydrides, the system pressure has to be lowered below the atmospheric pressure even at temperatures over $1,000^{\circ}$F.

Titanium, Zirconium, and Hafnium. Titanium hydride can be prepared by passing hydrogen over titanium at temperatures over 630°F--the temperature at which the hydride begins to form [44]--and cooling quickly. Sponge and ingot titanium absorb, respectively, a maximum of 42.96 and 38.14 liters of hydrogen per 100 grams of the metal. The compound obtained desorbs hydrogen at 570°F when heated in vacuum. McQuillan [45] and others [46, 47, 48] have studied the titanium-hydrogen system extensively and developed the pressure-temperature-composition diagrams which show that the dissociation pressure of the hydride is below atmospheric pressure even at temperatures approaching $1,600^{\circ}$F.

Zirconium reacts with hydrogen readily forming hydrides with composition varying between $ZrH_{1.33}$ and ZrH_2. Because of the good thermal stability of zirconium hydride, it has been extensively studied for nuclear reactor applications, particularly as a moderator. For the purpose of this survey, only two references [49, 50] need be cited in which the pressure-temperature-composition curves have been reported at pressures up to slightly above atmospheric pressure. These curves show conclusively that temperatures of over $1,800^{\circ}$F are required to liberate any hydrogen from zirconium hydride. This observation make the use of zirconium for hydrogen storage applications impractical. For essentially the same reason, hafnium [22] is also not useful for hydrogen storage applications.

Copper, Silver, and Gold; Zinc, Cadmium and Mercury. Solubility of hydrogen in copper, silver, and gold is very low, and increases slightly with temperature. The solubility of hydrogen, in atoms of hydrogen per atom of metal, even under the most favorable conditions does not exceed 8×10^{-4} in copper, 0.42×10^{-4} in silver, and even less in gold [19]. The hydrides of zinc, cadmium, and mercury cannot be prepared from direct reaction of hydrogen with the metal because the solubility is very low. None of these metals, therefore, is suitable for hydrogen storage applications.

Boron, Aluminum, Gallium, Indium, and Thallium. The solubility of hydrogen in boron is negligible. Boranes are therefore prepared through chemical reactions in solution. Various hydrides of boron are either gaseous at room temperature or are low-boiling-point liquids. Boron

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hydrides are, therefore, not suitable for hydrogen storage applications. The solubility of hydrogen in aluminum, gallium, indium, and thallium is too low to be of any interest for the application under consideration.

Silicon, Germanium, Tin, Lead, Chromium, Molybdenum, Tungsten, Manganese, Technetium, and Rhenium. The solubility of hydrogen in silicon, germanium, tin, lead, chromium, molybdenum, tungsten, manganese, technetium, and rhenium is too low to be of any practical value in hydrogen storage applications.

Iron, Cobalt, Nickel, Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum. The reaction of hydrogen with iron, cobalt, and nickel is endothermic, and the solubility is too low to be of any practical consequence. The solubilities of hydrogen in ruthenium, rhodium, osmium, iridium, and platinum are also too low to be of any use for hydrogen storage applications. Palladium is the only metal in this group which absorbs hydrogen in appreciable quantity. It forms a hydride of the formula $PdH_{0.6}$ to $PdH_{0.7}$. The palladium-hydrogen system has been very extensively studide by a number of researchers and a number of publications are available for review [19]. Based upon two of these studies [51, 52], one can see that the concentration of hydrogen in palladium at atmospheric pressure is low and decreases with increasing temperature, the atomic ratio varying between 0.0419 at $280^{\circ}F$ and 0.0077 at $1,870^{\circ}F$. To obtain higher compositions, the system pressure has to be increased. At $620^{\circ}F$, the atomic ratio of hydrogen to palladium increases from 0.426 at 50 atmospheres to 0.691 at 990 atmospheres. Since system pressure in practical applications may be limited to about 50 atmospheres, the atomic ratio of hydrogen to palladium may be limited to only about 0.43.

Since mixtures of metals, discussed later, absorb far more hydrogen at lower system pressures, are less expensive, and are easily available, palladium does not appear to be attractive for hydrogen storage applications.

Arsenic, Antimony, Bismuth, Selenium, and Tellurium. Arsenic hydride, antimony hydride, and bismuth hydride are gaseous, and, therefore, unsuitable for this application. There is no information available on selenium and tellurium hydrides, presumably because these elements do not form hydrides readily.

Vanadium, Niobium, and Tantalum. These metals readily absorb hydrogen at atmospheric pressure and room temperature to form stable hydrides of the stoichiometric formula MH, although in most cases these hydrides are hydrogen deficient [9] and [53 through 55]. Reilly and Wiswall [30] have been successful in preparing higher hydrides of vanadium and niobium of approximate composition MH_2 by direct absorption of hydrogen by the metal. All attempts to prepare tantalum hydride beyond the composition $TaH_{0.9}$ have so far been unsuccessful [30].

The higher hydrides of vanadium and niobium of approximate composition VH_2 and NbH_2 are relatively unstable. By decreasing the system pressure to atmospheric at about $100^\circ F$, the vanadium dihydride gives up some of the hydrogen slowly and stabilizes at a composition of $VH_{0.88}$. Further release of hydrogen from $VH_{0.88}$ at atmospheric pressure is possible if its temperature is raised substantially. For instance, raising the temperature to about $775^\circ F$ will reduce the hydrogen to metal ratio to 0.27, whereas a temperature of $1,100^\circ F$ is required to further reduce this ratio to 0.062 [9].

The hydriding behavior of niobium is similar to vanadium in most respects. By decreasing the system pressure to atmospheric at about $100^\circ F$, niobium dihydride gives up hydrogen until the hydrogen-to-metal atomic ratio reaches about 1.1. Raising the temperature of the system could further release hydrogen until the hydrogen-to-metal ratio reaches about 0.15 at $1,100^\circ F$ [9].

It is more difficult to release hydrogen from tantalum hydride. At atmospheric pressure, the temperature of the hydride has to be raised to about $785^\circ F$ to reduce the hydrogen-to-metal ratio from 0.9 to 0.38.

The dissociation pressures in each of the above three cases could be raised if small amounts of catalytic metals are added to pure metals prior to hydriding. This aspect will be discussed in the intermetallic section of this report.

A hazard of these hydrides, which have dissociation pressures of 1 atmosphere or greater at ambient temperatures, is that they generally will release hydrogen when exposed to the atmosphere. If a fire is allowed to start it can burn the hydrogen which is further released by the heat.

Because these metals are expensive, are not widely available, are hazardous, give up hydrogen below the hydrogen-to-metal ratio of 0.9 only with difficulty, and absorb and release hydrogen more readily in the presence of catalysts, pure vanadium, niobium, and tantalum are not considered suitable for hydrogen storage applications.

Summary. No pure metal appears completely suitable for the hydrogen storage applications under consideration. The pure metals are either too stable, or they don't hold enough hydrogen; they are either not widely available and thus cost a great deal, or they react too slowly with hydrogen. On the other hand, as described in the next section, some intermetallic compounds have recently been discovered which absorb and release hydrogen very easily, are not very expensive, and are widely available.

Hydrides of Intermetallic Compounds

In recent years many intermetallic compounds have been tested to determine their hydrogen storage capabilities. As mentioned earlier this search has been rewarded by the discovery of several satisfactory

compounds which will store large amounts of hydrogen at useful pressures and which will release this hydrogen with the addition of low to medium quality heat (100° to 600°F). As is often the case, each of these compounds presents problems, and some compounds appear to be better suited for particular applications than others.

Table 2 has been compiled to show most of the intermetallic hydrides which were included in the literature surveyed. Others have been studied [59]; but there was either too little information available, or they were of less interest than those shown. Included in this table is the percentage by weight of hydrogen in each of these compounds. Also included are statements of serious problems that would make a listed compound undesirable. The four single metallic compounds magnesium, vanadium, niobium, and palladium have been included for comparison.

A major problem with most transportable hydrogen storage systems is their weight. A heavy system requires that more energy be used to move it than does a light system; thus, a light system is more desirable than a heavy system. The percentage-by-weight figures in Table 2 can be used to judge the weights of the systems. A low percentage indicates that more of that particular compound will have to be carried to provide the same amount of hydrogen as a compound with a higher percentage. Table 3 includes those compounds which have a 1% or better hydrogen content. Table 3 provides several vital points of information on each of these compounds, when available, along with some comparative figures to provide a basis for judging among the compounds.

The vital information that have previously been published are the density, the hydrogen-atom-to-formula ratio, the dissociation enthalpy, and the plateau pressure and temperature charts. Information still needed for the design of a heat exchanger includes the thermal conductivity and the rates of hydrogen absorption and desorption. From the information available, the hydrogen density for a system with no voids can be derived as is the case with the hydrogen weight fraction and comparative values for the weight and volume of containers capable of holding an amount of hydrogen with a lower heating value equivalent to that of 10 gallons of gasoline.

The properties of the four single-element hydrides listed in Table 2 and of the liquid and compressed hydrogen without their containers are also included in Table 3.

The cost estimates of each of these compounds are based on small quantities, as given in the 1974-75 Ventron chemicals catalog [66], and compared to bulk price estimates obtained from the Molybdenum Corporation of America. The Molybdenum Corporation of America estimates that mischmetal-pentanickel can probably be provided at a cost of about $5 per pound which is one-half of its present large-lot cost. The assumption that has been made is that lanthanum pentanickel will also be available at one-half of its present $25.00 per pound large-lot price. By comparing this price to the price that the Ventron Corporation would charge for the constituent materials a factor of 5.96 was obtained. The prices of the other compounds were found by first calculating the cost of the constituents of 1 pound of the compound and then dividing by the factor 5.96.

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Table 3.

Item	Liquid H_2	Pressurized H_2		$Mg + 6\%$ Ni	$Mg + 9\%$ Cu	Fe Ti	
		2,000 psia	7,600 psia				
Density (lb/ft^3)	4.42 [63]	0.76 [63]^d	2.6 [63]^d	100	100^f	362	240
(gm/cm^3)	0.0700	0.12 [63]^d	—	1.6^e	1.6^f	5.8 [57]	3.85 [3
H_2 density (lb H_2/ft^3) (void fraction = 0)	4.42	0.764	2.6	6.7	5.9	6.9	3.6
Weight fraction (lb H_2/lb compound)	1.00	1.00	1.00	0.067	0.059	0.019	
Atom ratio (atoms H/formula unit)	—	—	—	2.0 [32]	1.88 [56]	1.9	
ΔH_{298} (Btu/lb mole H_2)	-30,600	-8,800	-13,000	-33,000	-33,660	-14,500	-13,
(Kcal/gm mole H_2)	-17.0^g	-4.9^b	-7.3^b	-18.5 [32]	-18.7 [56]	-8.06 [57]	-7.1
Working temperature $^\circ$F	-423 [63]	70	70	620	620	104	
$^\circ$C	-253	21	21	320 [32]	320 [56]	40 [57]	
Plateau pressure (psia)	14.7 [63]	2,000	7,500	44-147	44-147	118-221	
at working temp (Atm)	1.0	136	510.2	3-10 [32]	3-10 [56]	8-15 [57]	
For Energy Equivalent to 10 Gallons of Gasoline^i							
Weight of hydride (lb)	21.2	21.2	21.2	317	360	1,061	
(Kg^k)	9.6	9.6	9.6	144	163	481	
Volume of hydride (ft^3)	4.8	27.8^j	8.1^j	3.2	3.6	3.1	5.9
(void fraction = 0) (m^3)	1.5	8.5	2.5	1.0	1.1	0.9	1.8
Cost estimate^k ($/lb)	—	—	—	1.1	1.2	2.5	
Stability at 70°F	boils	high pressure		stable	stable	stable	
Problems	needs insulation	requires heavy tanks for storage		high temp high ΔH_{298}	high temp high ΔH_{298}	low wt % H_2	

^{a} Constants used in calculations.

Fuel	Lower Heating Value [65] (Btu/lb)	Density (lb/ft^3)
Gasoline	19,500	42 = 5.6 lb/gal [65]
Hydrogen gas	51,600	0.0056 at 70°F, 1 atm [63]
Hydrogen liquid	51,600	4.42 at -423°F, 1 atm [63]

^{b} Reference 35 reports that La Ni$_5$ H$_{6.7}$ has an apparent density of 3.85 gm/cm^3 but could possibly be compressed to 6.74 gm/cm^3.

^{c} Mm refers to mischmetal.

^{d} Calculated from data provided in the reference indicated by the number in the brackets.

^{e} Estimate of density based on densities of Mg H$_2$ at 1.4 gm/cm^3 [11] and of Mg$_2$ Ni H$_4$ at 2.54 gm/cm^3 [32].

^{f} Assumed to be similar to Mg + 6% Ni.

^{g} Liquefaction of hydrogen quantity of energy equal to 30 to 49% of energy stored in L H$_2$ [7].

^{h} Assumes that electrolytic hydrogen produced at 300 psig and 250°F [5] is compressed by a compressor with an isentropic efficiency of 0.9 [64] to the desir

^{i} 1 gallon gasoline = 109, 200 Btu = 2.12 lb H$_2$ [65].

^{j} From Perfect Gas Law.

^{k} Based on data from Reference 66.

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erties of Various Compounds that May Be Used for Metal Hydride Storage[a]

	Hydrides of —								
b	La$_{0.7}$Ce$_{0.3}$Ni$_5$	Mm Ni$_5$[c]	Zr Ni	VNb	Ce Mg$_{8.5}$	La Mg$_{8.5}$	Y$_5$ Mg$_{24}$	La Cu Ni$_4$	M
41B	–	–	400	–	–	–	–	–	87.
6.74 [35]	–	–	6.38 [60]	–	–	–	–	–	1.4
6.27	–	–	4.0	–	–	–	–	–	6.
5	0.016	0.015	0.010	0.0125	0.045 [23]	0.053 [23]	0.048 [28]	0.0114	0.0765
8]	7.0 [58]	6.5 [28]	1.5 [60]	1.8 [61][d]	–	–	–	5.0 [28]	2.0
-21,600	–	–	-33,120	–	–	–	–	–	-32...
.0 [58]	–	–	-18.4 [60]	–	–	–	–	–	-17.8
:	.	-18 to 122	572	158	620	620	620	122	62
8]	–	-28 to 50 [23]	300 [60]	70 [61]	320 [28][d]	320 [28][d]	320 [28][d]	50 [28]	320
'	–	44 to 588	29.4	58.8	74	88	88	30	44-1
tJ	–	3 to 40 [77]	2 [46][d]	4 [94]	5 [28][d]	6 [28][d]	6 [28][d]	2 [28]	3-10
5	1,326	1,415	2,122	1,698	471	400	442	1,860	27
:	601	642	963	770	214	181	200	844	12
3.4	–	–	5.3	–	–	–	–	–	3.
1.0	–	–	1.6	–	–	–	–	–	1.
;	12.0	5.0	3.5	20.5	15.7	15.0	41.8	12.4	1.
:H$_2$	releases H$_2$	releases H$_2$	–	–	unstable	unstable	unstable	–	stab
6 H$_2$ sice	low wt % H$_2$ high price	low wt % H$_2$ high price	low wt % H$_2$	low wt % H$_2$ high cost	pyrophoric	pyrophoric	pyrophoric high cost	low wt % H$_2$	po kine-

re.

b

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ides of –

	VNb	Ce Ni3.5	La Mg8.5	Y5 Mg24	La Co Ni4	Mg	V	Nb	Pd
	–	–	–	–	–	87.4	144	418	750
	–	–	–	–	–	1.4 [11]	2.3 [62]^d	6.7 [62]	12.02 [63]
	–	–	–	–	–	6.7	2.79	3.59	3.54
	0.0125	0.045 [28]	0.053 [28]	0.048 [28]	0.0114	0.0765 [27]	0.0194	0.0086	0.0047
	8 [61]^d	–	–	–	5.0 [28]	2.0 [26]	1.0 [62]	0.8 [62]	0.5 [51]
	–	–	–	–	–	-32,040	-17,316	-17,208	-15,948
	–	–	–	–	–	-17.8 [27]	-9.62 [62]	-9.56 [62]	-8.86 [9]
	158	620	620	620	122	620	129	133	392
	0 [61]	320 [28]^d	320 [28]^d	320 [_8]^d	50 [28]	320 [26]	54 [62]	56 [62]	200 [51]
	58.8	74	88	88	30	44-147	118	44-132	59
	4 [94]	5 [28]^d	6 [28]^d	6 [28]^d	2 [28]	3-10 [26]	8 [62]	3-9 [74]	4 [51]
	1,698	471	400	442	1,860	277	1,094	2,467	4,500
	770	214	181	200	844	126	496	1,119	2,041
	–	–	–	–	–	3.2	7.6	5.9	6.0
	–	–	–	–	–	1.0	2.3	1.8	1.8
	20.5	15.7	15.0	41.8	12.4	1.1	19.0	21.3	600
	–	unstable	unstable	unstable	–	stable	unstable	stable	--
	low wt % H2 igh cost	pyrophoric	pyrophoric	pyrophoric high cost	low wt % H2	poor kinetics	pyrophoric	low wt % H2	high cost

Magnesium-nickel Hydride. The magnesium-nickel hydrides contain the largest percentage by weight of hydrogen of any hydride so far studied. An alloy of 94% magnesium and 6% nickel can hold as much as 6.97 percent by weight of hydrogen when in its hydride form. This hydride was first investigated in the late 1960's by Drs. J. J. Reilly and R. H. Wiswall, Jr. [32], who have reported that the kinetics of this hydride are satisfactory and improve with temperature. As in most cases, though, there is no reported data on the rates of absorption and generation.

This hydride has several good points and several drawbacks; the drawbacks do not appear insuperable, however. The benefits are that a large amount of hydrogen can be stored at low pressure, at low temperature, with a low weight (compared to all other known intermetallic hydrides) and with a relatively low volume. Table 3 shows that 21.2 pounds of hydrogen, which can be burned to produce the same amount of energy as 10 gallons of gasoline, can be stored in 317 pounds and 3.17 cubic feet of magnesium-nickel hydride. It can also be seen that this volume is less than the volume required to store liquid hydrogen, 4.8 cubic feet. In actuality, the volume required in the hydride system would be greater due to spaces left between the granules of the hydride and due to the spaces required in the heat exchanger. These spaces determine the void fraction. However, even if the actual volume were twice as large, it would only be a little greater than liquid hydrogen.

The major drawback of this hydride is that a temperature of about 600°F must be maintained to release the hydrogen from the hydride and to maintain a satisfactory rate of absorption and generation. This medium temperature heat is frequently available in combustion engines and combustion exhausts, but there generally is not enough of this high quality energy. One possible solution is to burn a part of the hydrogen produced to heat the exhaust products and thus to provide the necessary extra energy. Another possibility is to design for a higher exhaust temperature. Though these methods may at first appear to be intensive energy users, a further look will reveal that metal-hydride systems allow the energy available in hydrogen to be more completely used. In a pressurized hydrogen storage system the hydrogen can be burned in an engine, but the exhaust products are released to the atmosphere, carrying with them a great deal of usable energy. A magnesium-nickel-hydride system, on the other hand, will produce hydrogen which can similarly be burned but the exhaust products can then be reheated slightly and passed through the hydride heat exchanger. Thus, some of the excess energy normally lost can be used to release more hydrogen. When the hydrogen is replenished this heat is given off by the hydride and can be used to provide the energy for an absorption cooling system or for heating systems.

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Magnesium-copper Hydride. The magnesium-copper hydride, also investigated by Drs. Reilly and Wiswall [56], has many characteristics similar to the magnesium-nickel hydride. It can hold 6.62 percent of weight of hydrogen and appears to have satisfactory kinetics at 600°F. Similar to the magnesium-nickel hydride, the magnesium-copper hydride has a large dissociation enthalpy. Generally, magnesium-copper hydride is a second choice to the magnesium-nickel hydrides and, as such, would only be used in cases when nickel was in short supply. As in the case of the magnesium-nickel hydride, data concerning the absorption and generation rates is lacking.

Iron-titanium Hydride. If a hydride which operates well at temperatures slightly above room temperature is needed, then iron-titanium hydride is probably the best that will be found. The price that is paid is in the weight. About 3.3 pounds of iron titanium must be used to store the same amount of hydrogen as can be stored in 1 pound of magnesium-nickel hydride. About half as much heat is required to release that hydrogen, though; and the heat that is required can be of a lower quality.

Investigated by Drs. Reilly and Wiswall [57] in the early 1970's, iron titanium has proven to be a promising hydride for hydrogen storage. It is about 3.6 times denser than magnesium-nickel hydride so it would take 3 cubic feet and 1,060 pounds of iron-titanium to store 21.2 pounds of hydrogen. The combination of this extra weight and an estimated cost of about twice that of magnesium nickel makes the cost of an iron-titanium system about six times that of magnesium nickel. These costs are estimates; and, due to the great availability of the constituent metals, the costs should not rise due to shortages. In fact if new and cheaper processes are developed for refining the metals, then the price should drop.

Lanthanum-pentanickel Hydride. Lanthanum-pentanickel (La Ni$_5$) hydride was investigated in the 1960's by J. H. N. Van Vucht, F. A. Kuijpers and H. C. A. M. Bruning of the Phillips Research Laboratory in Eindhoven, Netherlands [58]. This hydride delivers a desirable pressure at room temperature, though the reaction rate at this temperature is slow. The reaction rate can be greatly improved by increasing the temperature. Reference 58 indicates that at a temperature of 120°F (49°C) the hydrogen can be 95% desorbed in just 3 minutes, whereas at a temperature of 64°F (18°C) the hydride is only 80% desorbed after 40 minutes. Thus, the desorption rate of the hydride can be controlled by controlling its temperature. This was the only hydride on which this type of data was available.

A look at Table 3 will show that the dissociation enthalpy is not a firmly known value. Phillips Research Laboratory has indicated the upper and lower values of this range; the actual dissociation enthalpy is unclear [58].

There are also two values listed in Table 3 for the density of lanthanum-pentanickel hydride. Reference 35 states that the lattice structure of this hydride changes with the addition of hydrogen to take

up a less compact configuration. Thus, during a complete transition
from $LaNi_5$ to $LaNi_5H_{6.7}$, Reference 35 gives the apparent density of the
fully expanded compound as 3.85 gm/cm^3 and then points out that if the
hydride could be compressed to eliminate voids it should have a density
of 6.74 gm/cm^3. This last figure is derived by assuming that the lattice
structure expands 25% without fracturing. These two values have been
included in Table 3 to indicate the hydrogen densities for both the
actual and the theoretically possible cases.

With all of the previous hydrides, contact with CO_2, CO, H_2O, or
O_2 will deactivate the hydride; lanthanum-pentanickel, however, is able
to absorb hydrogen from gas mixtures containing these other gases. This
ability may make lanthanum-pentanickel and some related compounds conten-
ders with palladium for hydrogen purification applications.

The only real disadvantages of the lanthanum-pentanickel hydride
are its low fraction of hydrogen and its high cost. This hydride
contains a maximum of 1.5% hydrogen by weight. Thus, to store 21.2
pounds of hydrogen one would need 1,415 pounds of the compound which would
cost $17,687 at $12.50 per pound. This would result in a volume of 5.89
cubic feet or 3.38 cubic feet, depending on whether one used the low or
the high density. The weight and cost are, therefore, major obstacles
in the use of this hydride for general mobile use.

Lanthanum-cerium-pentanickel Hydride. Van Vucht, et al. [58] point
out that by adding a small amount of cerium to create a compound of
$La_{0.7}Ce_{0.3}Ni_5$, seven atoms of hydrogen can be combined with each formula
unit instead of the 6.7 atoms that $LaNi_5$ is able to hold. This mixture
was shown to be the optimum-cerium-lanthanum mixture for holding hydrogen;
and, since cerium is cheaper than lanthanum, the economics are better,
too. It would take 1,320 pounds of this compound to store 21.2 pounds
of hydrogen at an estimated cost of $15,840--an improvement but still
too expensive.

Mischmetal-pentanickel Hydride. Another cousin to the lanthanum-
pentanickel is mischmetal-pentanickel. Mischmetal is a term which describes
a mixture of several rare-earth metals. The mixture is fairly uniform
containing 50% cerium, 27% Lanthanum, 16% Neodymium, 5% Praseodymium,
and 2% other rare-earth metals. This hydride delivers hydrogen at 2
atmospheres at $-24^\circ F$ ($-31^\circ C$); thus, it can conceivably take the heat it
needs for dissociation from its surroundings.

Like the $LaNi_5$, this hydride can be used to absorb hydrogen from
impure gas mixtures; but also, like $LaNi_5$, the weight needed to store
21.2 pounds of hydrogen is 1,415 pounds. Again, the weight is a problem.
The Molybdenum Corporation of America estimates that in volume this
hydride can be supplied for $5.00 per pound which would mean that a
21.2-pound hydrogen storage unit would cost about $7,075.

Zirconium-nickel Hydride. Of all the hydrides shown on Table 3,
zirconium-nickel hydride stores the least amount of hydrogen, 1% by
weight. Reported in 1957 by George G. Libowitz, Herbert F. Hayes, and

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Thomas R. P. Gibb, Jr. [60], zirconium-nickel hydride has a dissociation enthalpy and a plateau temperature and pressure similar to that of magnesium-nickel, but it can hold only a small fraction of the hydrogen that magnesium-nickel holds. In addition, it costs about three times more per pound. Thus, zirconium-nickel hydride appears to have all the disadvantages of magnesium-nickel hydride with none of the advantages.

Vanadium-niobium Hydride. Not much is presently written about vanadium-niobium hydride. This report relies on the paragraph included in Reference 61. From this information one can see that this hydride contains only 1.25% hydrogen and that nearly 1,700 pounds of vanadium-niobium hydride would be needed to store 21.2 pounds of hydrogen. In Figure 7b one can see that vanadium-niobium hydride has a dissociation plateau of 4 atmospheres at $158^{\circ}F$ $(70^{\circ}C)$. A consideration of cost shows that one should not expect a cost of much less than \$20 per pound. This hydride, then, can probably be discarded from consideration as a hydrogen storage system due to its high cost and heavy weight.

$CeMg_{8.5}$, $LaMg_{8.5}$, Y_5Mg_{24}. The next three intermetallic hydrides listed in Table 3 were studied by Drs. Reilly and Wiswall and reported in 1972. They are mentioned because they all contain fairly high percentages by weight of hydrogen. They have dissociation pressures and temperatures similar to magnesium hydride and are all expensive. In addition, they are all pyrophoric and therefore, generally undesirable.

$LaCuNi_4$. This hydride is a variation of the lanthanum-pentanickel hydride. It was investigated by Drs. Reilly and Wiswall [28] in 1971-2. As shown in Table 3, it has dissociation plateaus similar to lanthanum-pentanickel, but it stores only 1.14% hydrogen by weight and thus requires a larger amount of hydride to store the same amount of hydrogen--1,860 pounds of hydride to store 21.2 pounds of hydrogen. As such, it has no advantages over lanthanum-pentanickel.

Vanadium with Impurities. Not mentioned in Table 3 is the intermetallic hydride of vanadium with impurities. Drs. Reilly and Wiswall have ascertained [62] that an impure vanadium will form a hydride with a higher dissociation pressure than a pure vanadium. This fact was discovered when the results of experiments made on a hydride of zone-refined vanadium were compared to those made on a hydride of commercial-grade vanadium. Further, it was shown that the less pure vanadium reacts faster with hydrogen. Other characteristics are the same as zone-refined vanadium, so only the zone-refined characteristics included in Table 3.

Vanadium hydride suffers the problems of being expensive and containing a very low percentage weight of hydrogen.

Summary. The best hydride storage medium in terms of cost and weight appears to be the magnesium-nickel hydride. In terms of volume, judgment is difficult because the void fraction is unknown and the heat exchanger volumes will depend upon

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the heat transfer properties of the materials. A magnesium-nickel hydride system for hydrogen storage costing between $500 and $700, weighing about 500 pounds, and taking up a volume equivalent to the volume occupied by a liquid hydrogen Dewar holding the same amount of hydrogen appears feasible, however.

Figure 1 provides a visual comparison of two hydride alternatives with gasoline and liquid and gaseous hydrogen. Figure 1a compares these systems in terms of costs. For the hydrides the costs include the costs of the containments and the metal hydrides. For the other systems the costs include only containers. Figure 1b compares the systems in terms of weight, and Figure 1c compares them in terms of volume. A 60% void fraction is assumed for the hydrides, but as mentioned earlier the void fraction is presently unknown. Figures 5 through 7 are pressure-composition graphs taken from the literature.

USES OF METAL-HYDRIDE STORAGE SYSTEMS

It has been determined that hydrogen is an excellent fuel, that it can be stored in relatively small volumes at low pressures by using metal hydrides or intermetallic hydrides, and that many hydrides exist with several ranges of applicability. Now some applications can be considered.

Remote-Base Energy Storage

In situations where volume is at a premium and where hydrogen is generated by wind, sea, or solar energy, metal hydrides can provide an excellent storage unit. In cases such as these, one would not want to waste hard-won energy in compressing hydrogen to high pressures, in liquifying and maintaining it at low temperatures, or in chemically synthesizing methane or methanol. A system where the hydrogen could be utilized at a relatively low pressure and temperature is highly desirable. Metal hydrides and large volume tank storage are presently the only systems that can provide this type of storage.

Combat Zone Energy Storage

In combat zones where construction time is limited or where invisibility is important, a low volume, easily transportable system would be invaluable. Metal hydrides can store hydrogen in volumes similar to the volume of liquified hydrogen; and the weight, though large, would not be too great to handle.
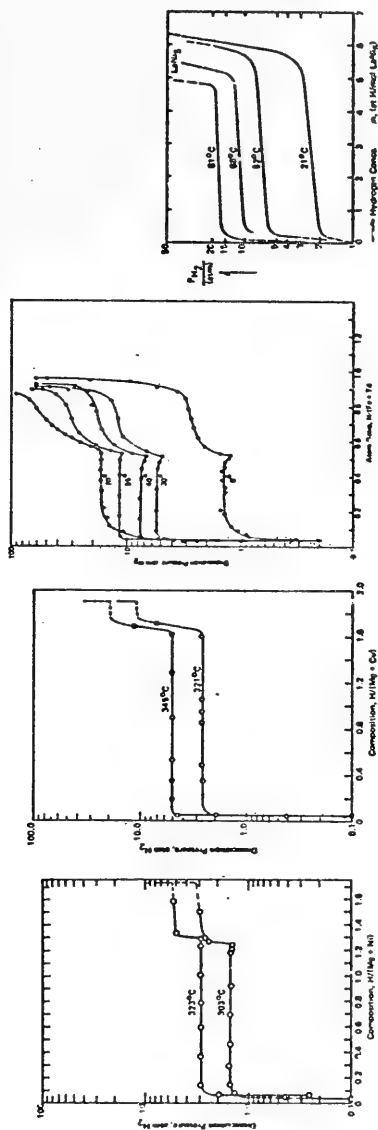
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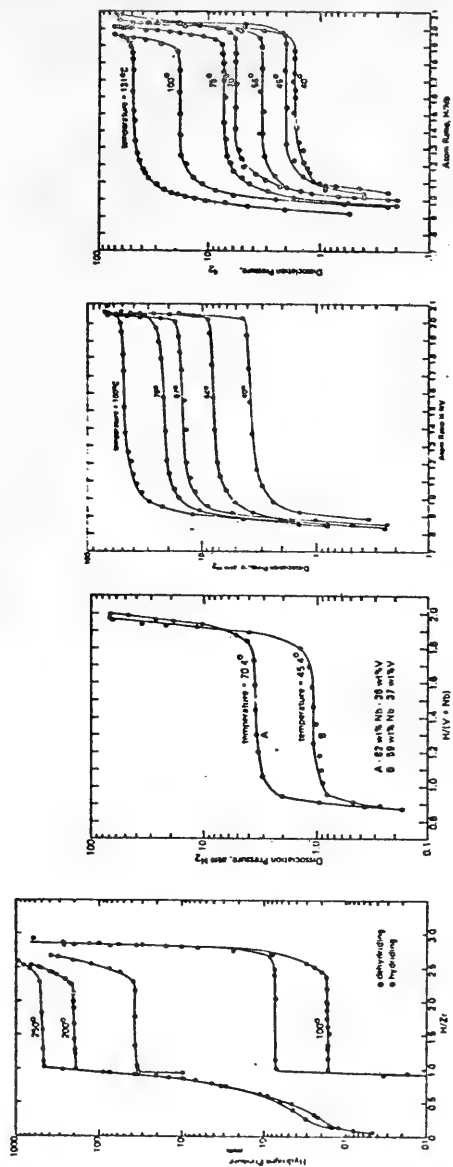Figure 5. Pressure-composition isotherms for the most promising metal-hydrogen systems.

Figure 6. Pressure-composition isotherms of various rare earth-hydride systems. These curves are from Reference 28, Hydrogen storage and purification systems, by J. J. Reilly and R. H. Wiswall, Jr., Brookhaven National Laboratory and are printed with its permission.

Figure 7. Pressure-composition isotherms for several metal-hydride systems.

Underwater Fuel Storage

Another Navy need is fuel storage for underwater facilities. A system can be envisioned where an underwater facility is supplied by two hoses: one carrying hydrogen and the other carrying oxygen or air. Small metal hydride units could be used to supply and store hydrogen for mobile units and for the container itself. Other methods would be used to store the oxygen or air. Fuel cells could supply any necessary electric power to the facility, and the heat given off during hydrogen absorption could be used to heat the facility. A small hydride container could be carried (along with an oxygen bottle, perhaps) to provide the hydrogen and oxygen for a fuel cell which would generate power for a mobile unit. In the case of a breakage in the umbilical tube, the facility could continue to function on stored oxygen and hydrogen.

Heat and Fuel Storage for a Closed-Cycle Engine

One solution to the problem of energy storage and waste heat disposal for installations such as in Project Sanguine[b] is the use of hydrogen for fuel and metal hydrides for storage. Since the metal hydrides must absorb heat during the generation of hydrogen, this heat can be supplied by the exhaust products of combustion. The products of combustion of hydrogen and oxygen are just heat and water, thus the additional problem of toxic gases is eliminated. Metal hydrides can be chosen to absorb most of the excess heat so that only a small amount would have to be disposed of in other ways.

Mobile Heat and Fuel Storage

For mobile systems which have access to atmospheric oxygen, only the metal hydride would need to be carried. Such systems could generate hydrogen using the exhaust heat from the engine itself or if fuel cells were being used, a small amount of the hydrogen produced could be burned to produce the needed heat for the desorption of the hydrogen. During recharge the heat released by the absorption of the hydrogen could be used to heat buildings or water or to run an absorption cooling process. In this way the available energy would be used more completely, first by heating the buildings or water during the absorption step and second by producing hydrogen to power engines during the desorption step.

Heat Pump

As shown in Appendix A, an analysis indicates that metal hydrides may provide a means to pump heat more efficiently than present-day heat pumps. One method of accomplishing this is with two hydride containers.

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[b] Navy's underground communication system.

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One would generate hydrogen along a low temperature-pressure dissocia-
tion plateau. The heat for this generation could be taken from the
outside atmosphere. The hydrogen thus released would be compressed to
a pressure that would cause the second hydride unit to absorb the
hydrogen at a temperature-pressure plateau above the room temperature.
This second container would release heat at this elevated temperature
which could be transferred to the room air, thereby warming the room.
The only power necessary for the system would be used by the compressor
to pressurize the hydrogen.

Appendix A shows the analysis of this system. An expression for
the coefficient of performance is the final result of the analysis. The
coefficient of performance can be visualized as the ratio of the amount
of heat delivered into the house per unit of energy used to deliver it.
The best heat pumps have the highest coefficients of performance.

Once the expression for the coefficient of performance was found,
typical values were assumed for the isentropic compressor efficiency and
the temperatures and pressures of the components of the system. A
typical isentropic compressor efficiency is 90%. The atmospheric tem-
perature was assumed to be 40°F. To promote a heat flow to the low
temperature hydride, the hydride was assumed to be absorbing heat at
such a rate that it maintained a temperature of 30°F. The compressor
output pressures were assumed at several values to see how this affected
the coefficient of performance. The table shown at the end of Appendix
A is the result of these calculations. It can be seen that the highest
coefficients of performance are obtained when the compressor output
pressures are low. This makes sense because less energy will be spent
to compress the hydrogen. A typical present technology heat pump can be
expected to have a coefficient of performance of 2 to 3 [65, 67]. Thus,
if pressures can be kept low it is conceivable that a superior heat pump
could be built using metal hydrides.

PROBLEMS AND SOLUTIONS

Several problems occur with each of the above systems. The problems
center around how to heat the hydride during generation of the hydrogen
and how to cool the hydride during absorption of the hydrogen. In
heating the hydride, the most desirable system will use a minimum of the
fuel. The most preferable situation uses only exhaust products to heat
the hydride. In cooling the hydride the most desirable system will use
the heat generated to perform some other task such as heating water,
heating buildings, providing processed steam, or supplying the heat
needed for an absorption cooling system. Thus, the hydride system
appears capable of squeezing more useful energy out of each pound of
fuel than would normally be the case.

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Heating Systems

As was mentioned in the section describing uses of metal-hydride storage, the heat needed to desorb hydrogen from the hydride can be supplied by exhaust gases and cooling water if the hydrogen is used in a combustion process; or it can be provided by burning some of the hydrogen. The following analyses consider only the thermodynamics of the problems. The full design of heat exchangers has not been attempted due to the lack of information concerning the chemical interactions of the hydrides with other metals, the density and thermal conductivity of the metal hydrides, and the necessary pressures and temperatures needed to provide desirable kinetics of absorption and desorption.

In considering using heat derived from the exhaust gases and cooling water, certain assumptions must be made. If the end use of the hydrogen is in an internal combustion engine, a fair assumption is that 30% of the energy derived from burning the hydrogen will be lost in the exhaust gases and 30% will be lost through the cooling system. Representative temperatures for these systems are 1,400°F at the exhaust manifold and 180°F at the cooling water exit from the engine.

Two methods of heating the hydride have been considered. In the first, fluids are allowed to blow over and around tubes containing the hydrides to accomplish the heating and cooling requirements. In the second, the tubes containing the hydrides are closely packed and hydrogen circulating through the hydrides performs the heating and cooling requirements.

Figure 8 shows these concepts more clearly. The first concept is shown in Figure 8a. The hydride is stored in tubes (I) which provide a containment capable of withstanding the pressures required during absorption of the hydrogen. The tubes are closed at one end and open at the other. The open ends are fixed to a tube plate (II). On the other side of the tube plate a domed cavity (III), designed to withstand the necessary pressures, provides a collection space for the hydrogen. A valved tube passing through the dome provides the entrance and exit port for the hydrogen. Hot gases or liquids can be passed through ports (IV) in the thin shell surrounding the tubes. The hot gases or liquids are then passed over and around the tubes in several passes guided by baffles. The heat from the gases or liquids flow through the tubes to a cooler hydride which upon absorption of the heat releases hydrogen. The hydrogen then is allowed to collect in the domed cavity at a pressure slightly above atmospheric from which it is ejected into the engine.

In the second concept (Figure 8b), the hydride is again contained in tubes which provide the necessary pressure containment. In this concept, however, the tubes are packed close together, thus reducing the size of the hydride containment component. The heat transfer is accomplished by hydrogen which is pumped through the hydride. The hydrogen is heated or cooled in a heat exchanger as the need arises. During times when hydrogen must be withdrawn from the hydride, heat is supplied to the hydrogen—from the exhaust gases, perhaps. Then the hot hydrogen

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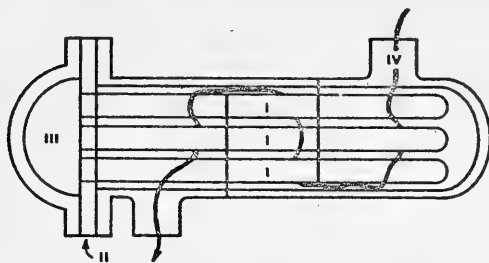
(a) Tubes are spaced so that gas flows evenly over each one.
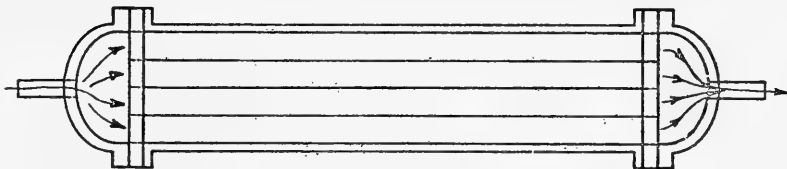
(b) Tubes are closely packed.

Figure 8. Metal-hydride/container concepts.

is pumped through the hydrides which absorb energy and give off more hydrogen which flows with the original cooler hydrogen out of the hydride containment and back to the heat exchanger finishing its closed cycle. Hydrogen can be tapped from this system downstream from the hydride containment.

The heat needed for these processes can be supplied from the exhaust gases, the cooling water (provided the dissociation temperature is low enough), from burning hydrogen, concentrated solar radiation, or from a combination of these methods. As shown in Appendix B (Heating Analysis section) there is an insufficient amount of high quality heat in the exhaust gases of a typical internal combustion engine to release the amount of hydrogen needed in the engine when magnesium nickel hydride is used. This has proven to be the major problem with the magnesium-nickel hydride. Sufficient heat is available to supply the dissociation energy for the iron-titanium hydride, however; and a combination system of some magnesium-nickel hydride and some iron-titanium hydride looks very promising. An optimization analysis to find the minimum possible weight for a dual system is planned but has yet not been executed. Alternatively, the system might be cheaper and lighter by burning part of the

hydrogen released by the hydride to provide the extra heat needed by the magnesium-nickel hydride. An analysis for this is also planned but not yet executed. This system might be necessary in situations where there is no combustion.

Cooling Systems

Using the two basic concepts described earlier (the gas flowing over tubes and hydrogen flowing through the tubes) the hydride can be cooled. In cooling as in heating more problems arise with magnesium-nickel hydride than with iron-titanium or lanthanum-pentanickel. Two factors must be taken into account in cooling these hydrides: the temperature at which the hydride must be maintained and the rate at which the hydrogen must be absorbed. Different methods must be used to cool a hydride that must be maintained at a temperature above the boiling point of water than to cool one which can be cooler. More problems arise in a system that has to be cooled in a very short period of time than in one which is allowed a longer time.

For iron-titanium and lanthanum-pentanickel the problems are similar because the temperatures are similar, and the most advantageous system would appear to be similar to the first concept. Large amounts of water can be passed over the tubes which contain the hydride and the heat carried away in the form of heated water. The period of time needed for the recharge can be varied by increasing or decreasing the rate of water passing over the tubes and the rate of hydrogen passing into the tubes. The heated water can then be used where heat is needed elsewhere. If a long period is available for recharge, air can be blown over the tubes and used for forced air heating.

For magnesium-nickel hydride, where the temperatures are higher, water could be sprayed into the containment with forced air thus creating a steam of about $250°$ to $300°F$. This steam could be used for many purposes including water heating and building heating. It would be hot enough to run absorption cooling systems. Calculations show that approximately 2 gallons of water would be boiled for every pound of hydrogen absorbed. This method could be used in both fast and slow recharge conditions. In the slow recharge condition air could be blown over the tubes and used for forced air heating. A better method might be to use the second concept though. In this method hydrogen would be added through the access port and passed with the circulating hydrogen through a heat exchanger where it is cooled. Then it would be pumped through the hydride container where it would both absorb heat and be partially absorbed by the hydride. The advantage of this system is that the hydrogen would moderate so that the hydride would not get too cold and thus slow its absorption rate. Water could be sprayed in the hydrogen heat exchanger in this system also, to produce a mild grade steam.

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CONCLUSIONS

The overall conclusions of this study are that there are no single element hydrides with satisfactory characteristics for the applications considered in this report. Of the many intermetallic hydrides that have so far been studied, the magnesium-nickel hydride appears to be the cheapest to produce and the lightest in weight. Magnesium-copper hydride is the next best, followed by iron-titanium hydride. A more expensive, but low-temperature alternative, is provided by the various rare-earth pentanickel hydrides with the mischmetal-pentanickel hydride providing acceptable storage characteristics at the lowest temperature. It must be emphasized that the figures for unit costs of the hydrides listed in Table 3 are estimates and are subject to increases and decreases dependent on the availability of the materials.

The survey of literature concerning these hydrides indicates that the rates of desorption of hydrogen from them is consistent with the needs of automotive engines and can be controlled sufficiently for the many uses for which hydrides can be envisioned.

A brief study was made of possible alternative fuels. This study showed that hydrogen is a very versatile fuel, nontoxic, and of use in making all of the other synthetic fuels. Energy can be conserved in practically every instance by using hydrogen rather than other alternative fuels. Next in line of the possible alternative fuels are methanol and ethanol.

Of the four methods for storing hydrogen, the metal hydride method weighs more than liquified hydrogen and its container but less than pressurized hydrogen and its container. In terms of volume the liquid and metal hydride systems are about the same and both are much less bulky than the pressurized system or the low pressure tank storage system. In short, for transportation purposes, pressurized and tank hydrogen can be ruled out. Thus the question is whether it is better to liquify the hydrogen and contend with all the problems that liquid hydrogen brings out or to carry more weight made up of the hydride material and have the ease of using a gaseous hydrogen.

The benefits of liquid hydrogen are that it is light and fairly compact. Its disadvantages are that (1) the energy needed to perform the liquifaction is equal to about one-third of the stored energy, (2) under normal conditions the lock up time for liquid hydrogen is only a few days, and (3) transporting and distributing liquid hydrogen is difficult.

In looking at gaseous hydrogen and metal hydrides the disadvantages are its weight and, in the case of magnesium-nickel hydride, its temperature. In the metal hydride system, the advantages distinctly outweigh the disadvantages. Refueling is fairly simple, requiring only a cooling system which can use the heat for other purposes and a source of low-pressure hydrogen. The lockup time is indefinitely long, depending only on the contamination rate of the hydride. The energy needed to release the hydrogen is also about one-third of the amount of stored energy but it is returned during recharge.

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Finally, several uses of metal hydrides have been suggested and several conceptual designs of heating and cooling systems have been made.

RECOMMENDATIONS

Considering the great usefulness and applicability of hydrogen as a fuel and the ability of metal hydrides to store hydrogen at low pressures and with little energy loss, it is recommended that:

1. Experimental work be performed to determine the thermal conductivities, actual densities, maximum rates of hydrogen absorption and desorption, and chemical properties of the hydrides of magnesium-nickel, iron-titanium and mischmetal-pentanickel. Containment tube materials should also be tested to determine their compatability with the hydrides.

2. An experimental heat-exchanger/hydride-container be designed and built to demonstrate the principles and to define the problems of a metal-hydride/hydrogen-storage system.

3. A prototype model be built for the application deemed most useful and capable of success in operation. The applications to be considered are hydrogen and heat storage for Sanguine systems, underwater facilities, remote stations, and transportation vehicles.

Hydrogen is a universal fuel for all applications including heating, cooling, transportation, and electric-power generation. Metal hydrides presently look like the best possible hydrogen storage method but the systems need further development.

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Appendix A

METAL HYDRIDE HEAT PUMP SYSTEM ANALYSIS
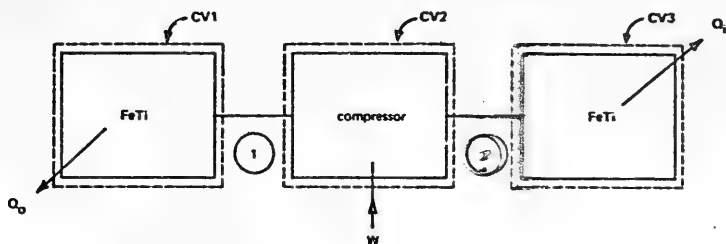
Definitions — ROCE   rate of creation of energy
ROCM   rate of creation of mass
STE   Storage of energy
STM   Storage of mass.

For the control volumes, the conservation statements are:

CV1

$$ROCE = 0 = Q_0 - \dot{m}_1 h_1 + \frac{d}{dt} (STE1) \qquad (1)$$

$$ROCM = 0 = -\dot{m}_1 + \frac{d}{dt} (STM1) \qquad (2)$$

CV2   idealizations: steady flow
adiabatic

$$ROCE = 0 = \dot{m}_1 h_1 - \dot{m}_2 h_2 - W \qquad (3)$$

$$ROCM = 0 = \dot{m}_1 - \dot{m}_2 \qquad (4)$$

CV3

$$ROCE = 0 = \dot{m}_2 h_2 - Q_1 + \frac{d}{dt} (STE3) \qquad (5)$$

$$ROCM = 0 = \dot{m}_2 + \frac{d}{dt} (STM3) \qquad (6)$$

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Given 1. ΔH_{298} = -7200 Btu/lbm H_2 (The dissociation enthalpy of FeTi) $\quad$ (7)

2. Typical isentropic efficiency for compressor = 0.90 $\quad$ (8)

Thus $\quad \dfrac{d}{dt}$ (STE3) = $\dot{m}_2$ (7200) $\quad$ (9)

$\dfrac{d}{dt}$ (STE1) = $\dot{m}_1$ (-7200) $\quad$ (10)

from 4 $\quad \dot{m}_1 = \dot{m}_2$ $\quad$ (11)

from 3 $\quad \dot{m}_1 h_1 - \dot{m}_2 h_2 = W$ $\quad$ (12)

from 11, 12 $\quad \dot{m}_1 (h_1 - h_2) = W$ $\quad$ (13)

from 1 $\quad Q_c = \dot{m}_1 h_1 - \dfrac{d}{dt}$ (STE1) $\quad$ (14)

from 10, 14 $\quad Q_o = \dot{m}_1 h_1 + \dot{m}_1$ (7200) $\quad$ (15)

from 13, 15 $\quad$ COP $= \dfrac{Q_c}{W} = \dfrac{\dot{m}_1 (h_1 + 7200)}{\dot{m}_1 (h_1 - h_2)} = \dfrac{(h_1 + 7200)}{(h_1 - h_2)}$ $\quad$ (16)

Now using the typical isentropic compressor efficiency

$$\varepsilon = 0.9 = \frac{h_{1s} - h_2}{h_1 - h_2}$$

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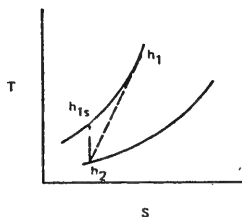
So $h_1 = h_2 + (h_{1s} - h_2)/0.9$

Assuming that $T_{atm} = 40^{\circ}F$

$$T_2 = 30^{\circ}F \qquad P_2 = 1 \text{ atm}$$

$$P_1 = 20, 30, 60, \text{ and } 70 \text{ atm.}$$

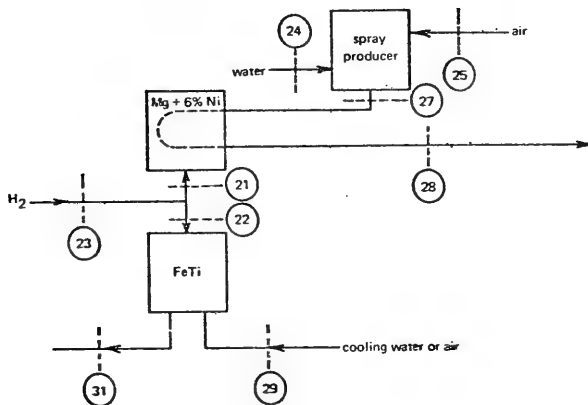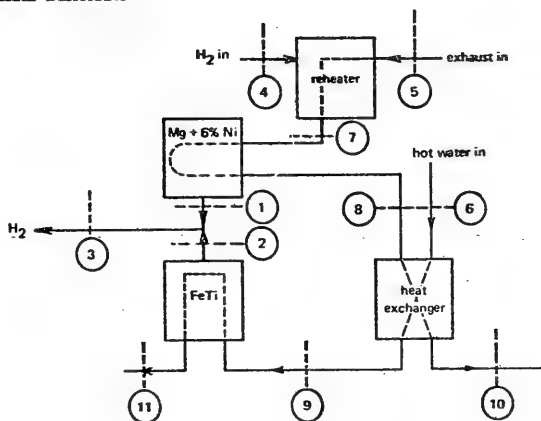a table can be compiled using values taken from Reference 68

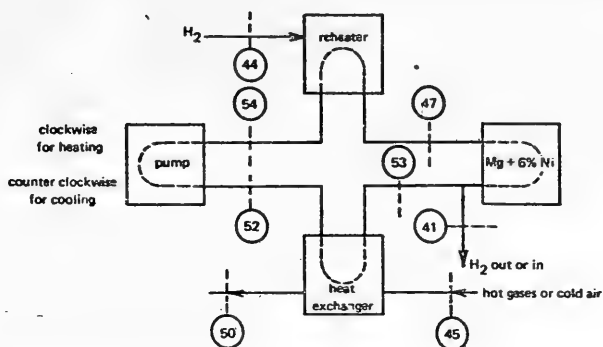| P_2	$\tilde{h}_{1s}$	h_{is}	h_1 Btu/lbm	$Q_o/W = COP$
20	7915	3926.1	4179.5	4.5
30	8898.4	4413.9	4721.5	3.9
60	10878.8	5396.2	5813.0	3.1
70	11378.0	5643.8	6088.1	3.0

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Appendix B

HEATING-COOLING SYSTEM ANALYSIS
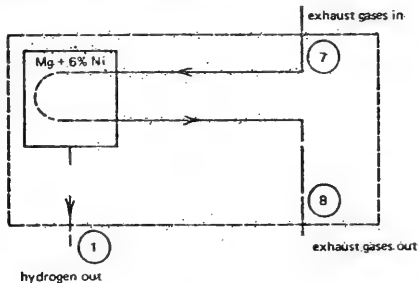
GENERAL DIAGRAMS

HEATING ANALYSIS

An Energy Balance showing that the exhaust gases from a typical internal combustion engine are insufficient to release the necessary hydrogen from magnesium-nickel hydride.

From the general diagram on H_2 generation.

Rate of Creation of mass $= 0 = \dot{m}_8 + \dot{m}_1 - \dot{m}_7 -- \dot{M}$

where $\dot{m}$ stands for mass per unit time passing across the dotted boundary of the control volume

and $\dot{M}$ stands for the rate of increase of mass in the control volume.

Rate of Creation of energy $= 0 = \dot{m}_8 h_8 + \dot{m}_1 h_1$

$$- \dot{m}_7 h_7 + \frac{d}{dt} (\text{Storage})$$

where h stands for the enthalpy of the $\dot{m}$ and d/dt (storage) stands for the rate of increase of energy storage.

Assume

      a. $1.4\ H_2 + O_2 + 3.76\ N_2 \rightarrow 1.4\ H_2O + 0.3\ O_2 + 3.76\ N_2$

      b. $T_7 = 1400^\circ F$

      c. $T_1 = 600^\circ F$

      d. $T_8 = 600^\circ F$ which implies that the hydride heat exchanger is 100% effective.

From <u>Gas Tables</u> by Keenan and Kaye [68], in terms of Btu/lb-mole

at T_7 $h_{H_2O} = 16027.6$ | at T_8 $h_{H_2O} = 8595.0$ | at T_1 $h_{H_2} = 7284.4$

          $h_{O_2} = 13986.8$ $h_{O_2} = 7543.6$

          $h_{N_2} = 13426.5$ $h_{N_2} = 7407.2$

Letting d/dt (storage) be the difference between the heat entering the hydride container and that leaving the hydride container.

$$\frac{d}{dt}\ (\text{storage}) = \dot{m}_7 h_7 - \dot{m}_8 h_8 - \dot{m}_1 h_1$$

$$= 1.4\ (16027.6 - 8595.0) + 0.3\ (13986.8 - 7543.6)$$

$$+ 3.76 (13426.5 - 7407.2) - 1.4 (7284.4)$$

$$= 24773 \frac{Btu}{lb\text{-}mole}$$

Therefore $\dfrac{24773.0 \; Btu}{1.4 \quad lb\text{-}mole \; of \; H_2} = \dfrac{17695 \; Btu}{lb\text{-}mole \; H_2}$ are available

in the exhaust gases of a hydrogen combustion process for absorption in the Mg Ni Hydride. From Table 3 it can be seen that Mg Ni hydride requires 33,300 Btu/lbmole of H_2. Thus 15,605 Btu more are needed to release every lbmole of H_2. There is not enough energy in the exhaust gases to release the hydrogen.

COOLING ANALYSIS

Calculations showing the water needs for boiling water cooling of magnesium-nickel hydride during hydrogen absorption.

Given   3 cases-Supply water at $60^{o}F$, $150^{o}F$, or $212^{o}F$
             final state is vapor at $250^{o}F$, 1 atmosphere.
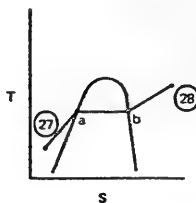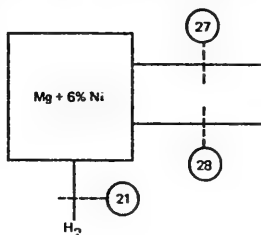
$$Q = (h_a - h_{27}) + (h_b - h_a) + (h_{28} - h_b)$$

$$= 14.5 \; lbm \; water \quad when \; T_{27} = 60^{o}F$$

$$15.7 \; lbm \; water \quad when \; T_{27} = 150^{o}F$$

$$17.0 \; lbm \; water \quad when \; T_{27} = 212^{o}F$$

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